

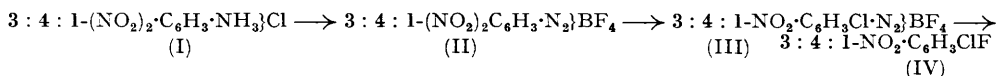
604. *The So-called "1-Fluoro-3 : 4-dinitrobenzene."*

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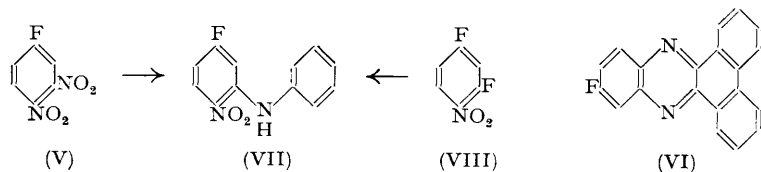
The so-called "1-fluoro-3 : 4-dinitrobenzene" (4-fluoro-1 : 2-dinitrobenzene) which Cannoni de Degiorgi and Zappi (*Anal. Asoc. Quím. Argentina*, 1940, **28**, 72) obtained by a Balz-Schiemann reaction on 3 : 4-dinitroaniline hydrochloride has been shown to be identical with 1-chloro-4-fluoro-2-nitrobenzene, the 4-nitro-group being replaced by chlorine during the diazotisation. The true 4-fluoro-1 : 2-dinitrobenzene has been prepared by nitration of *m*-fluoronitrobenzene, and its structure confirmed.

CANNONI DE DEGIORGI and ZAPPI (*Anal. Asoc. Quím. Argentina*, 1940, **28**, 72) have assigned to a yellow substance of m. p. 34° which they obtained by a Schiemann reaction on 3 : 4-dinitroaniline hydrochloride (I) the structure of 4-fluoro-1 : 2-dinitrobenzene (V) and to the intermediate borofluoride that of (II).

Analytical figures for substance (II) were not quoted, nor was an analysis for nitrogen given for (V). Since 4-fluoro-1 : 2-dinitrobenzene was needed for a wider investigation, this preparation was repeated; it gave a substance of similar physical properties (m. p. 35°) but of the formula $C_6H_3O_2NClF$, one of the nitro-groups having been replaced by chlorine. The exchange had not taken place during formation of the hydrochloride, because 3 : 4-dinitroaniline could be recovered from its salt. Since, however, the diazonium borofluoride contained chlorine, it was concluded that the replacement reaction had occurred during the diazotisation. Cannoni de Degiorgi and Zappi's compound was identified as 1-chloro-4-fluoro-2-nitrobenzene (IV), m. p. 35.9° (Ingold and Vass, *J.*, 1928, 2262), by a mixed-melting-point determination with an authentic specimen. The Schiemann reaction on 3 : 4-dinitroaniline (I) in hydrochloric acid leads, therefore, to the borofluoride (III) which, on pyrolysis, gives the chloro-compound (IV).



Expulsion of a nitro-group by chlorine during diazotisation has been recorded by, *e.g.*, Meldola and Eyre (*J.*, 1901, 1077) for polynitroanisidines, and Schiemann and Ley (*Ber.*, 1936, **69**, 960) for 1-nitro-2-naphthylamine. In each case elimination of the nitro-group follows the formation of the positively charged diazonium group which, by virtue of its high electron-attracting effect ($-I$, $-T$) presumably renders the *ortho*- or *para*-position particularly vulnerable to the attack of a nucleophilic chlorine ion. It is of interest that diazotisation of 3 : 4-dinitroaniline in sulphuric acid does not lead to the replacement of a nitro-group.



The true 4-fluoro-1 : 2-dinitrobenzene (V) was readily obtained by nitration of *m*-fluoronitrobenzene. The nitration product possesses two adjacent nitro-groups, because reduction, followed by addition of phenanthraquinone, yielded phenanthrazine or 11-fluorophenanthrazine (VI; for numbering see Ring Index No. 3252), according to the conditions of the reaction. The position of the fluorine atom relative to that of the two nitro-groups is established by the fact that the same fluoronitrodiphenylamine (VII) resulted from the condensation of aniline with the fluorodinitrobenzene (V) or with 2 : 4-difluoro-1-nitrobenzene (VIII).

The use of the strongly nucleophilic piperidine for determination of structure (Le Fèvre and Turner, *J.*, 1927, 1113) also proved of diagnostic value, because treatment of compound (V) or (VIII) yielded the same 1-nitro-2 : 4-dipiperidinobenzene.

EXPERIMENTAL

Decompositions of diazonium borofluorides were carried out in a current of dry nitrogen. Boron trifluoride fumes were thereby readily removed. The inert atmosphere reduced the formation of phenolic by-products and rendered the decomposition of large quantities controllable.

The Alleged "1-Fluoro-3 : 4-dinitrobenzene" (1-Chloro-4-fluoro-2-nitrobenzene).—The method of Cannoni de Degiorgi and Zappi (*Anal. Asoc. Quim. Argentina*, 1940, **28**, 71) was followed, except for the hydrolysis of 3 : 4-dinitroacetanilide, which was carried out with ethanol (5 vols.)—concentrated sulphuric acid (1 vol.), which gave a cleaner product and a higher yield. The so-called "3 : 4-dinitrobenzenediazonium borofluoride" (4-chloro-3-nitrobenzenediazonium borofluoride), m. p. 158—159° (decomp.), gave a positive test for chlorine. Cannoni de Degiorgi and Zappi (*loc. cit.*) give "decomp. 161°." On pyrolysis it yielded a pale-yellow substance which crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 35° alone or mixed with 1-chloro-4-fluoro-2-nitrobenzene (see below) (Found : C, 41.0; H, 1.6; N, 7.9; Cl, 20.7. Calc. for $C_6H_3O_2NClF$: C, 41.0; H, 1.7; N, 8.0; Cl, 20.2%).

1-Chloro-4-fluoro-2-nitrobenzene (cf. Swarts, *Rec. Trav. chim.*, 1915, **35**, 131; Ingold and Vass, *J.*, 1928, 2262).—*p*-Chloroaniline (25 g.) was diazotised in aqueous (18%) hydrochloric acid (120 c.c.) with sodium nitrite solution (50%), and addition of sodium borofluoride solution (110 c.c. of 40%) precipitated colourless *p*-chlorobenzenediazonium borofluoride, m. p. 126° (decomp.) (35 g., 79%). Pyrolysis yielded *p*-chlorofluorobenzene, b. p. 130°/758 mm. (16 g., 80%). Swarts (*loc. cit.*) records b. p. 129.1—130.2°/757 mm. *p*-Chlorofluorobenzene (12.6 g.) afforded on nitration by Swarts's method (*loc. cit.*) a pale-yellow liquid mixture (13 g.) of 4-chloro-1- and 1-chloro-4-fluoro-2-nitrobenzene. This (5 g.) was warmed in alcoholic 0.1N-potassium hydroxide (82.5 c.c.) at 40° for $\frac{3}{4}$ hr.; conversion of the unwanted 4-chloro-1-fluoro-2-nitrobenzene into the corresponding chloronitrophenol was followed by titration of test samples (0.5 c.c.) with 0.1M-hydrochloric acid. When the titre no longer changed (40 min.), the mixture was neutralised with 0.01N-hydrochloric acid and extracted with ether. Evaporation of the dried ethereal extract afforded a pale-yellow solid, of m. p. 30° which could not be raised by recrystallisation. The substance (0.2 g.) was chromatographed in light petroleum (b. p. 60—80°; 100 c.c.) on alumina (activated alumina, P. Spence, Type H, 100—200 mesh; 1 × 10 cm.) with the solvent (420 c.c.) as eluant (50-c.c. fractions). From the final fractions nearly colourless 1-chloro-4-fluoro-2-nitrobenzene, m. p. 36°, was obtained on evaporation. Ingold and Vass (*loc. cit.*) give m. p. 35.9° (Found : C, 41.0; H, 1.8; N, 7.8; Cl, 20.4%).

4-Fluoro-1 : 2-dinitrobenzene.—(a) *m*-Fluoronitrobenzene (12.0 g.) (Schiemann and Pillarsky, *Ber.*, 1929, **62**, 3035) was added dropwise with stirring to a 1 : 1-mixture (130 c.c.) of nitric acid (*d* 1.5) and sulphuric acid (*d* 1.84). The mixture was kept at 50° for 0.5 hr. and then poured on ice (300 g.). The lemon-coloured solid was collected, washed with sodium carbonate solution (10%) until the wash-liquid was colourless, and then with water. Recrystallisation from ethanol and then light petroleum (b. p. 60—80°) afforded nearly colourless, prismatic needles (up to 3.5 cm.) of 4-fluoro-1 : 2-dinitrobenzene, m. p. 55—56° (13.2 g. crude; 11.4 g. pure, 74%) [Found : C, 38.8; H, 1.7; N, 15.1. $C_6H_3O_4N_2F$ requires C, 38.7; H, 1.6; N, 15.0%. Estimation of nitro-groups : 0.31 G. consumed 0.180 g. of $SnCl_2$. $C_6H_3F(NO_2)_2$ requires 0.185 g.

(b) Finely powdered 3 : 4-dinitroaniline (4.5 g.) (Wender, *Gazzetta*, 1889, **19**, 225) was triturated with 50% sulphuric acid (25 c.c.) and then diazotised with solid sodium nitrite at about -10°. Addition of sodium borofluoride solution (5.4 g., 40%) yielded pale-brown 3 : 4-dinitrobenzenediazonium borofluoride (2 g., 29%), decomp. 166—169°. Thermal decomposition afforded a pale-yellow solid (0.14 g., 10%), m. p. 54° alone or mixed with a specimen prepared as described under (a).

Phenanthrazine.—4-Fluoro-1 : 2-dinitrobenzene (0.5 g.) was reduced by Jones and Robinson's method (*J.*, 1917, 912) and then treated with a hot solution of phenanthraquinone (0.8 g.) in 50% aqueous sodium hydrogen sulphite solution (6 c.c.) buffered with sodium acetate (1 g.). A solid, m. p. 216°, separated which showed an undepressed m. p. when mixed with an authentic sample of phenanthrazine.

11-Fluorophenanthrazine.—4-Fluoro-1 : 2-dinitrobenzene (0.4 g.) was shaken in ethanol (20 c.c.) under hydrogen at room temperature and pressure in presence of Adams's platinum catalyst (50 mg.). After filtration the ethanol was evaporated off under diminished pressure, the residual solid was taken up in ether, and the hydrochloride of the base precipitated with dry hydrogen chloride. 4-Fluoro-*o*-phenylenediamine (0.19 g., 70.5%) was obtained by treatment of the salt with concentrated ammonia solution. It crystallised from benzene as greyish

needles, m. p. 88—89° (Found: C, 57.4; H, 5.3; N, 22.4. $C_6H_7N_2F$ requires C, 57.1; H, 5.6; N, 22.2%). A mixture of the diamine (0.1 g.) in ethanol (1 c.c.) and phenanthraquinone (0.17 g.) in acetic acid (2 c.c.), warmed for a few minutes, gave 11-fluorophenanthrazine as pale yellow flakes, m. p. 226° (Found: C, 80.7; H, 3.5; N, 9.3. $C_{20}H_{11}N_2F$ requires C, 80.5; H, 3.7; N, 9.4%).

5-Fluoro-2-nitrodiphenylamine.—(a) 4-Fluoro-1:2-dinitrobenzene (6 g.) and freshly distilled aniline (14.5 c.c.) were heated together on a steam-bath for 7 hr. with gradual addition of finely powdered sodium acetate (2.4 g.). The dark-red mixture was set aside at room temperature for 1 day and then poured into 20% hydrochloric acid (100 c.c.) to remove excess of aniline. The brown solid which separated was washed free from acid and recrystallised from ethanol. *5-Fluoro-2-nitrodiphenylamine* (4.8 g., 64.5%) separated as golden-yellow needles, m. p. 93—94° (Found: C, 62.2; H, 3.9; N, 12.1. $C_{12}H_9O_2N_2F$ requires C, 62.0; H, 3.9; N, 12.0%).

(b) A mixture of 2:4-difluoro-1-nitrobenzene (8.2 g.) (Schiemann, *J. pr. Chem.*, 1934, **140**, 97) and freshly distilled aniline (40 g.) was kept overnight at room temperature. (Alternatively the condensation could be effected by heating on a steam-bath for 0.5 hr.) An orange-red crystalline deposit appeared after 1 hr. The dark-red suspension was poured into a separator containing 20% aqueous hydrochloric acid (150 c.c.) and benzene (100 c.c.). The violet acid layer was run off and the brown benzene extract was repeatedly washed with 20% hydrochloric acid and finally dried. Evaporation of the solvent yielded a brown solid which was purified by steam-distillation and afforded 5-fluoro-2-nitrodiphenylamine (10 g., 84%) as lemon-coloured needles, m. p. 94° alone or mixed with a specimen prepared as described under (a).

1-Nitro-2:4-dipiperidinobenzene.—(a) To 4-fluoro-1:2-dinitrobenzene (0.5 g.), piperidine (2 c.c.) was added dropwise with cooling and, when the violent reaction had ceased, the mixture was boiled for 1 min. On addition of water (20 c.c.) an orange-coloured oil separated which, after being washed with water and dried in a desiccator, crystallised in contact with benzene. 1-Nitro-2:4-dipiperidinobenzene (0.5 g., 62%) separated from ethanol as orange-red needles, m. p. and mixed m. p. 63—64° (Found: N, 14.3. Calc. for $C_{16}H_{23}O_2N_3$: N, 14.5%). Le Fèvre and Turner (*J.*, 1927, 1113) give m. p. 63—64°.

(b) 2:4-Difluoro-1-nitrobenzene (0.5 g.) was treated with piperidine (2 c.c.) as described above, giving 1-nitro-2:4-dipiperidinobenzene (nearly quantitative yield), m. p. and mixed m. p. 63—64°